

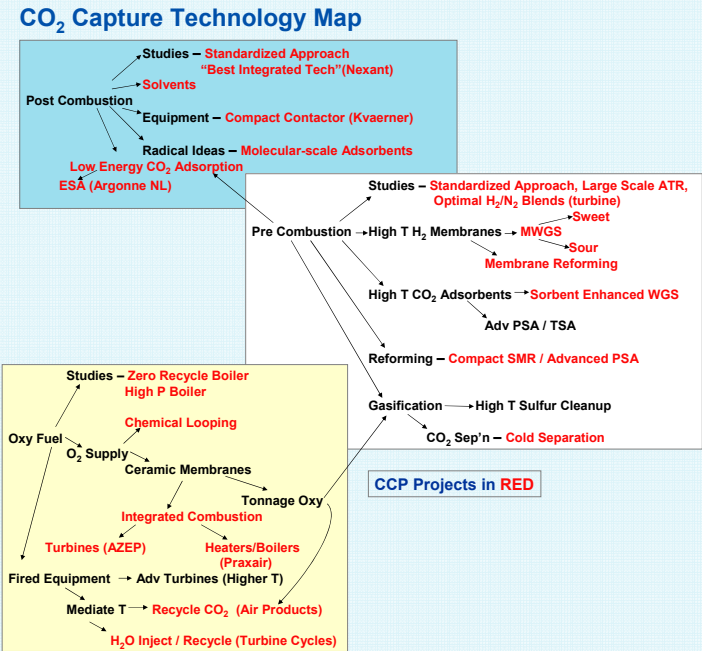
# The CO<sub>2</sub> Capture Project – Capture Technology Program for Phase 2

## Cooperating for a Better Environment The CO<sub>2</sub> Capture Project:

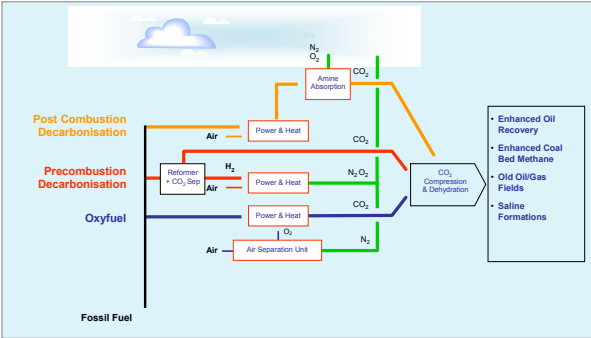
- Is an international industry/government partnership, including 8 of the world's leading energy companies and 3 governments.
- Develops BREAKTHROUGH TECHNOLOGIES to reduce the cost of CO<sub>2</sub> capture.
- Is a 3-phase program, just beginning Phase 2 (2005-2008), developing technology performance with \$25mm in funding.
- Working to demonstrate storage is safe, measurable and verifiable.
- Involving other interested parties in the NGO community.

## Phase 1 Accomplishments (2000–2004)

More than 100 technology ideas screened



## There are Three Broad Approaches to CO<sub>2</sub> Capture



## Phase 1 Results: Progress in Reducing Capture Costs

CCP has progressed the development of a range of technologies for Capture of CO<sub>2</sub>

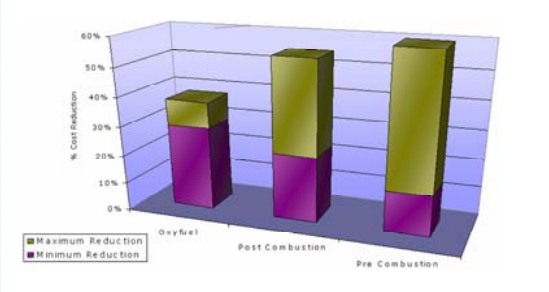
- Capture of CO<sub>2</sub> in exhaust gases from combustion sources, such as power plants. This technology can be retrofitted to existing equipment. (**Post-combustion**)

  - Membrane Contactor
  - Gas Turbines with Flue Gas Recycle
- Conversion of natural gas to hydrogen and burning of hydrogen, generating nitrogen and water with CO<sub>2</sub> captured for storage. (**Pre-combustion**)

  - Advanced Syngas Regeneration
  - Thermal Reforming
  - Hydrogen Membranes
  - Adsorbents
- Separation of oxygen from air and pure oxygen used to burn fuels, resulting in CO<sub>2</sub> for storage. (**Oxy-fuel combustion**)

  - High T Membrane Separation
  - Chemical Looping / Metal Oxide Redox Cycles

### Cost Reduction Achieved Relative to Status in Year 2000



## CCP Phase 2 Plans (2005–2008): Building on the Success of Phase 1

### Project Objectives for Phase 2

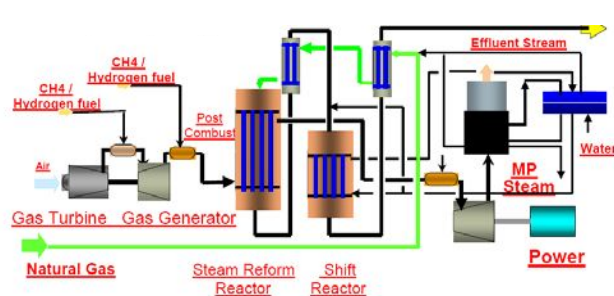
- Undertake additional research, development and pilot testing to reduce cost of CO<sub>2</sub> capture from large fixed sources.
- Reduce technology and cost uncertainty associated with those technologies and deliver low-cost CO<sub>2</sub> capture technologies to demonstration stage by 2009.
- Demonstrate that the geological storage of CO<sub>2</sub> is secure and can represent a viable Greenhouse Gas mitigation technique. Further develop technology, best practice and industry standards for storage site evaluation, risk assessment, well integrity, monitoring and verification.
- Establish an extended network for CO<sub>2</sub> storage demonstrations to share learning and best practice.

### Phase 2 Capture Goal:

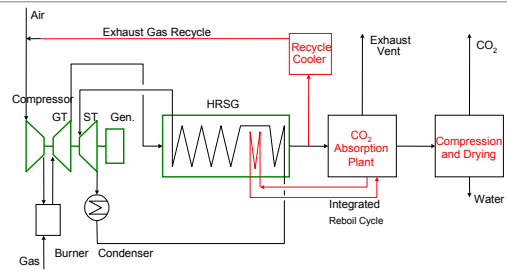
Further reducing costs of capture technologies to be ready for demonstration in 2009 with broad applications

Priority	Technology
Near Term	Sorption Enhanced Water Gas Shift Best Integrated Technology
Mid-term Priority	Chemical Looping
Long-term Priority	Hydrogen Membrane Reactor Novel Technologies

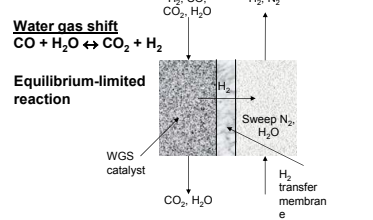
### Integrated SMR and Power Generation



### Best Integrated Technology for Power Gen or “BIT”



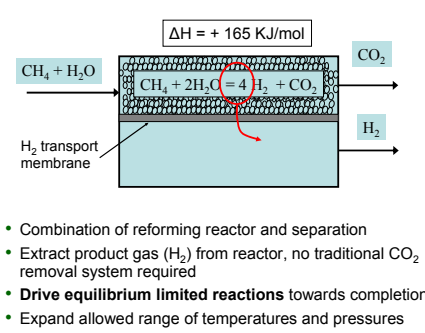
### MWGS Reactor Concept



### SEWGS Concept

- Uses high temperature CO<sub>2</sub> adsorbent in presence of WGS catalyst
- Drives equilibrium by “removing” CO<sub>2</sub>
- Regenerated by heating
- Cyclic bed concept

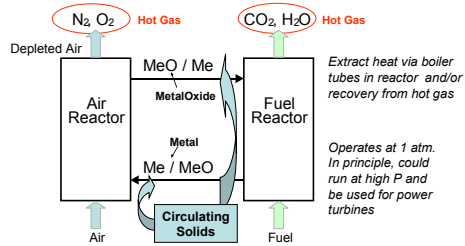
### H<sub>2</sub> Membrane Reformer Concept



- Combination of reforming reactor and separation
- Extract product gas (H<sub>2</sub>) from reactor, no traditional CO<sub>2</sub> removal system required
- Drive equilibrium limited reactions towards completion
- Expand allowed range of temperatures and pressures

### Chemical Looping Combustion

BASIC IDEA: Circulating solids that are alternately reduced and oxidized. This has the effect of transporting oxygen from the air reactor to the fuel reactor.



- CCP-funded work in Europe, led by Chalmers University (Sweden) and Altom Power, confirmed workability of chemical looping combustion
- Operated as an integrated pilot unit with NiO carrier at 30KW scale

### Chemical Looping Reforming or H<sub>2</sub> Production

- Extends the Chemical Looping concept to production of syngas or hydrogen
- One concept looks like CLC, but achieves partial oxidation to make syngas in the “fuel reactor”
- Another concept uses metal oxide that can be oxidized with steam, in order to produce H<sub>2</sub> directly

### Private/public project partners and co-funders:



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## Modeling CO2 plume evolution in oil reservoirs using parallel computing

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### Abstract

CO2 sequestration (capture, separation, and long term storage) in various geologic media (such as depleted oil reservoirs, saline aquifers, oceanic sediments) is a possible solution to reduce green house gas emissions. In this study we utilize the PFLOTTRAN simulator to investigate geologic sequestration of CO2. PFLOTTRAN is a massively parallel 3-D reservoir simulator for modeling subsurface multiphase (CO2, H2O), and multicomponent reactive flow and transport based on continuum scale mass and energy conservation equations. PFLOTTRAN has an efficient and modular mechanism to handle variable switching during multiphase transitions, bringing great flexibility in choosing the set of primary variables, addition of new EoS, mixing rules, etc. The multiphase flow equations are sequentially coupled to reactive transport equations describing multi-component chemical reactions within the formation. These reactions consist of aqueous speciation, and precipitation and dissolution of minerals including CO2-bearing phases to describe aqueous and mineral CO2 sequestration. The effect of the injected CO2 on pH, CO2 concentration within the aqueous phase, mineral stability, and other factors can be evaluated with this model. This work is focused on complex density driven flow patterns within both CO2-rich and aqueous phases, and their effect on the long-term containment of injected supercritical CO2. The efficiency of sequestration processes could be affected by many factors, including variations in fluid properties caused by CO2 dissolution and reservoir salinity, changes in geochemical and geophysical properties caused by mineral dissolution and precipitation, etc. This investigation will help provide criteria for site selection and to investigate leakage rates of CO2 to the surface.

### PFLOTTRAN: Parallel Flow and Reactive Transport

#### Mathematical Formulation

PFLOTTRAN consists of two distinct modules: a mass and energy flow code (PFLOW) and a reactive transport code (PTRAN). The module PFLOW solves mass conservation equations for water and other fluids and an energy balance equation. The module PTRAN solves mass conservation equations for a multicomponent geochemical system. The reactions included in PTRAN involve aqueous species and minerals which can be written in the general form:

$$\sum v_p A_i \rightleftharpoons A_j \quad \text{and} \quad \sum v_p A_i \rightleftharpoons M_n$$

respectively, where the set of species  $\{A_i\}$  refer to a set of primary or basis species in terms of which all other species are written.  $A_j$  denotes an aqueous complex referred to as a secondary species.  $M_n$  refers to a mineral, and  $v_p$  and  $v_m$  are reaction stoichiometric coefficients derived from an extensive database. The architecture is shown in the right figure.

#### Mass Conservation: Flow Equations

$$\frac{\partial}{\partial t} (\phi \rho_i p_i X_i^T) + \nabla \cdot [q_i \rho_i X_i^T - \phi \rho_i D_i^T \nabla X_i^T] - Q_i^T$$

$$q_i = -\frac{k_{rel,i}}{\mu} \nabla (p_i - W_{p,i} \rho_i g) \quad p_i = p_g - p_{i,g}$$

#### Energy Conservation Equation

$$\frac{\partial}{\partial t} [\phi \sum_i \rho_i U_i + (1 - \phi) \rho_r T] + \nabla \cdot [\sum_i q_i \rho_i H_i - \kappa \nabla T] - Q_r$$

#### Multicomponent Reactive Transport Equations

$$\frac{\partial}{\partial t} [\phi \sum_i v_i W_i] + \nabla \cdot [\sum_i q_i \rho_i W_i] - \sum_i v_i R_i = Q_i$$

#### Total Concentration

$$W_i^T = \partial_i C_i^T + \sum_j C_j^T$$

#### Total Solute Flux

$$Q_i^T = (-\phi \rho_i D_i^T \nabla + q_i) W_i^T$$

#### Mineral Mass Transport Equation

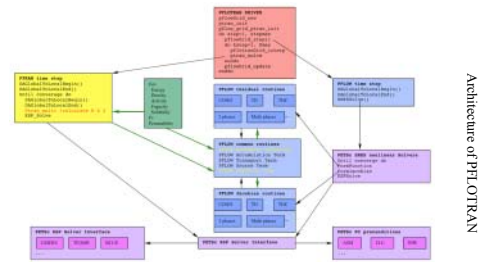
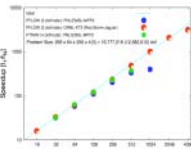
$$\frac{\partial \phi_i}{\partial t} = V_i J_i$$

$$\phi \times \sum_i \phi_i = 1$$

System closure is accomplished by combining these equations with other auxiliary equations and EoS of phases. Most current EoS, solubility and relative permeability formulae were implemented to ensure accuracy, such as Span-Wagner formula for supercritical CO2 phase properties, etc.

### Performance and scalability

PFLOTTRAN been designed from scratch with parallel scalability in mind, and it displays excellent scaling characteristics on modern supercomputers. The figure at right shows the performance of PFLOW running a one phase thermodynamic benchmark problem on a 256 x 64 x 256 grid with three degrees of freedom per node (approximately 12.6 million degrees of freedom total). The benchmark was run on both the MP22 cluster at PNNL/EMSL, a cluster of 1960 1.5 GHz Itanium 2 processors with Quadrics QsNe III interconnect, and Jaguar, the 5200 Opteron processor Cray XT3 at ORNL/NCNS. PFLOW scales quite well on both machines, bottoming out at around 1024 processors on MP22, and scaling exceptionally well on Jaguar, displaying linear speedup all the way up to 2048 processors, and still displaying modest speedup when going from there to 4096 processors.



### Variable switching and phase transition

PFLOW assumes all components exist in system are partly miscible. The solubility is governed by a modified Henry's Law. It employs the commonly used variable switching method to choose certain numbers of primary variables according to Gibbs phase law, resulting in  $n_{var} = n_{comp} + 1$ . With this method, the set of primary variables varies for every possible phase combinations in  $2^{n_{comp}} - 1$  cases, as listed in the table below. Other thermodynamic properties are derived from the primary variables through constraints and equilibrium relations.

Phase transition rules are one of the crucial aspects for implementing the variable switching method. A generic rule to determine if a new phase  $p$  forms is that the summation of all mole fractions in the new phase exceeds one, as evaluated from existing phases by pseudo equilibrium,  $\sum X_i^p > 1$ : a phase disappears if its saturation is less than zero,  $S_i < 0$ .

In the numerical implementation, a relaxation method is needed to reduce oscillations and improve performance. Examples below show phase transition diagrams for 3 and 4 phase systems and the selection of primary variables for a 3-phase 3-component system.

#### Example: 3 components (H2O, CO2, C10H22), 3 phases (Water, Supercritical CO2, oil) system

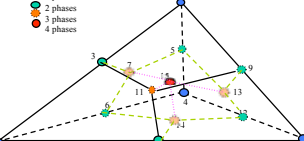
Case	Phase Condition	Primary Variables
1	W	P, T, $X_{CO_2}^{SC}$ , $X_{C_{10}}^{SC}$
2	G	P, T, $X_{CO_2}^{SC}$ , $X_{C_{10}}^{SC}$
3	W+G	P, T, $X_{CO_2}^{SC}$ , $X_{C_{10}}^{SC}$
4	O	P, T, $X_{CO_2}^{SC}$ , $X_{C_{10}}^{SC}$
5	O+G	P, T, $X_{CO_2}^{SC}$ , $X_{C_{10}}^{SC}$
6	O+W	P, T, $X_{CO_2}^{SC}$ , $X_{C_{10}}^{SC}$
7	O+W+G	P, T, $X_{CO_2}^{SC}$ , $X_{C_{10}}^{SC}$

#### Phase transition diagram



#### Example: 4 phase system (P1, P2, P3, P4), phase transition diagram

Case	Phase Condition	Case	Phase Condition	Case	Phase Condition
1	P1	6	P2 + P3	11	P1 + P2 + P4
2	P2	7	P1 + P2 + P3	12	P1 + P3 + P4
3	P1 + P2	8	P4	13	P1 + P3 + P4
4	P1	9	P1 + P4	14	P2 + P3 + P4
5	P1 + P3	10	P2 + P4	15	P1 + P2 + P3 + P4

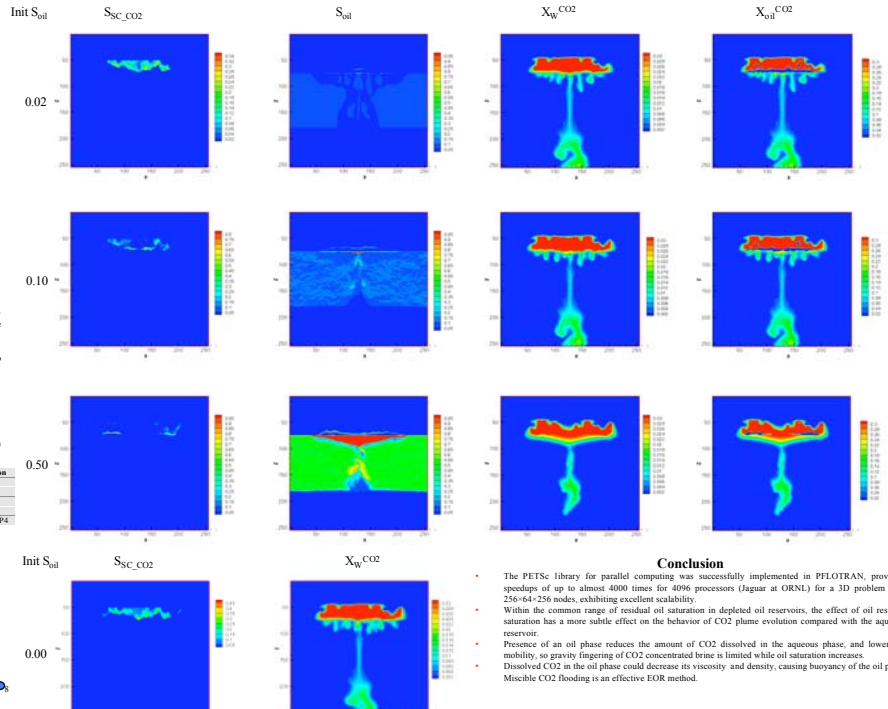
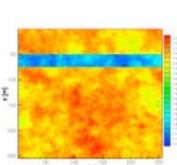


### Numerical Simulation

The simulation was conducted for a 2D domain with dimensions 256 x 256m on a uniform grid with 1 x 1m spacing using a random permeability field containing 3 uncorrelated layers with 50m, 25m and 101m thickness, from top to bottom. The log-normal distributed random field is generated by the sequential Gaussian random field generator  $\mu$ gfm from GSLIB, with correlation length 20 m, zero mean and variance 0.25. The values are scaled with the mean permeability of each layer with 10-2, 10-5, 10-2 Darcy, as shown on the right panel. CO2 is injected for 10 years with the rate 1.6x10-4 kg/s at the center of the domain at a depth of 140m.

The initial residual oil is located at depths ranging from 75m to 180m, horizontally across the whole domain. Four cases with different initial oil saturation (0, 0.02, 0.10, 0.50) are investigated. Outside the dominant oil region, the oil saturation is set to a small value (1x10-4), except for the first case, in which the oil residual is zero everywhere. The relative permeability is determined by linear interpolation. No capillary effect is considered.

Snapshots of saturation and concentration at 400 years are shown in the right panel.



### Conclusion

- The PETSc library for parallel computing was successfully implemented in PFLOTTRAN, providing speedups of up to almost 4000 times for 4096 processors (Jaguar at ORNL) for a 3D problem with 256-64x256 nodes, exhibiting excellent scalability.
- Within the common range of residual oil saturation in depleted oil reservoirs, the effect of oil residual saturation has a more subtle effect on the behavior of CO2 plume evolution compared with the aqueous reservoir.
- Presence of an oil phase reduces the amount of CO2 dissolved in the aqueous phase, and lowers its mobility, so gravity fingering of CO2 concentrated brine is limited while oil saturation increases.
- Dissolved CO2 in the oil phase could decrease its viscosity and density, causing buoyancy of the oil phase. Miscible CO2 flooding is an effective EOR method.

### Acknowledgements

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Distribution of CO2 in phases